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Published in:
Chemistry of Materials

DOI:
[10.1021/cm203351t](https://doi.org/10.1021/cm203351t)

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2012

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Van Mierloo, S., Hadipour, A., Spijkman, M.-J., Van den Brande, N., Ruttens, B., Kesters, J., D'Haen, J., Van Assche, G., de Leeuw, D. M., Aernouts, T., Manca, J., Lutsen, L., Vanderzande, D. J., Maes, W., & Haen, J. D. (2012). Improved Photovoltaic Performance of a Semicrystalline Narrow Bandgap Copolymer Based on 4H-Cyclopenta[2,1-b:3,4-b']dithiophene Donor and Thiazolo[5,4-d]thiazole Acceptor Units. *Chemistry of Materials*, 24(3), 587-593. <https://doi.org/10.1021/cm203351t>

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Improved Photovoltaic Performance of a Semicrystalline Narrow Bandgap Copolymer Based on 4*H*-Cyclopenta[2,1-*b*:3,4-*b'*]dithiophene Donor and Thiazolo[5,4-*d*]thiazole Acceptor Units

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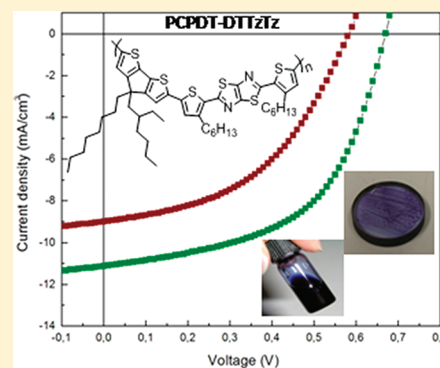
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S Supporting Information

ABSTRACT: A solution processable narrow bandgap polymer composed of alternating 2,5-dithienylthiazolo[5,4-*d*]thiazole and asymmetrically alkyl-substituted 4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene units (PCPDT-DTTzTz) was synthesized by Suzuki polycondensation and the donor–acceptor copolymer was thoroughly characterized. Thermal analysis and X-ray diffraction studies disclosed the semicrystalline nature of the material. When blended with PC₇₁BM and integrated in bulk heterojunction organic solar cells, a moderate power conversion efficiency of 2.43% under AM 1.5 G (100 mW/cm²) conditions was obtained. However, upon purification of the semiconducting copolymer by preparative size exclusion chromatography, a noticeable rise in power conversion efficiency to 4.03% was achieved. The purified polymer exhibited a relatively high field-effect carrier mobility of 1.0×10^{-3} cm²/(V s). The active layer morphology was explored by atomic force microscopy and transmission electron microscopy studies, showing phase segregation on the nanometer scale.

KEYWORDS: 4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene, thiazolo[5,4-*d*]thiazole, alkyl side chains, semicrystallinity, preparative GPC, bulk heterojunction organic solar cells



INTRODUCTION

Organic (polymer) solar cells (OSC's) offer great opportunities as renewable energy sources, as they combine unique features such as the potential for low cost large-area fabrication, solution processability, aesthetics, reduced weight, and mechanical flexibility.¹ Bulk heterojunction (BHJ) OSC's based on regioregular poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C₆₁ butyric acid methyl ester (PC₆₁BM) as active layer donor and acceptor materials, respectively, have achieved power conversion efficiencies (PCE's) of 4–5%.^{1–3} The main problem associated with the P3HT:PC₆₁BM combination is the

mismatch between the OSC absorption window and the terrestrial solar spectrum due to the relatively large bandgap of the polythiophene donor polymer and the limited absorption width of the material blend. The most popular approach to obtain lower bandgap structures is based on copolymerization of (heteroaromatic) donor and acceptor moieties.¹ Incorporating alternating electron rich and electron deficient subunits

Received: November 10, 2011

Revised: January 12, 2012

Published: January 13, 2012



produces a significant decrease in the bandgap (and a concomitant red-shifted absorption) due to intramolecular charge transfer (ICT).

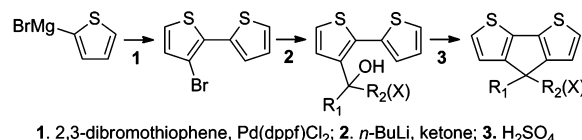
During the last five years, 4*H*-cyclopenta[2,1-*b*:3,4-*b'*]-dithiophene (CPDT) has emerged as an attractive building block for organic photovoltaics (OPV), combining good electron-donating properties, a rigid coplanar structure favoring π - π intermolecular interactions, and straightforward side-chain manipulation to influence solubility and processability. Although a standard workhorse material among the high efficiency low bandgap copolymers has not been defined yet, PCPDTBT, consisting of alternating CPDT and 2,1,3-benzothiadiazole (BT) units, is undoubtedly the most studied and best defined material within this subclass.^{4–15} Bazan and co-workers achieved a break-through result – a noticeable PCE improvement from 2.8 to 5.5% – for this polymer, carrying branched 2-ethylhexyl side chains, in combination with PC₇₁BM ([6,6]-phenyl-C₇₁ butyric acid methyl ester) upon processing with 1,8-octanedithiol.⁶ On the other hand, ultrahigh mobility (3.3 cm²/(V s)) has very recently been observed for a PCPDTBT copolymer bearing long linear alkyl side chains.¹¹ The crucial influence of the alkyl side chains and the polymer molecular weight, often underestimated in the past, on the opto-electronic properties have clearly been illustrated for this (and other) low bandgap material(s). The electron deficient thiazolo[5,4-*d*]thiazole (TzTz) entity has also been introduced as an interesting candidate for integration in organic electronics due to its strong electron-withdrawing properties, high oxidative stability, planar and rigid structure, and straightforward synthesis.^{16–29} In the OPV field, TzTz building blocks have become increasingly popular, noticeably during the last year. A number of donor–acceptor copolymer structures incorporating TzTz moieties as the electron poor units have appeared in the literature, showing rather high charge-carrier mobilities and PCE's.^{19–29}

Combination of both attractive building blocks in a low bandgap copolymer is evidently a promising approach. Shim et al. already reported cyclopentadithiophene-*co*-thiazolothiazole copolymers (PehCDT-Tz) with a hole mobility of 1.1×10^{-4} cm²/(V s) and an average PCE of 2.23% when blended with PC₆₁BM.¹⁹ Based on synthetic experience within the group on both monomeric precursors,^{30,31} the design and synthesis of an alternative more performant 'PCPDT-TzTz' derivative were pursued. Here, we report the synthesis and physicochemical properties of a novel narrow bandgap copolymer, poly([4-(2'-ethylhexyl)-4-octyl-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene-2,6-diyl]-*alt*-[2,5-di(3'-hexylthiophen-2'-yl)thiazolo[5,4-*d*]thiazole-5',5'-diyl]) or PCPDT-DTTzTz, composed of asymmetrically dialkylated CPDT units and hexyl-substituted dithienyl-TzTz moieties in an alternating fashion. After blending the polymer with PC₇₁BM as an electron acceptor in a 1:3 w/w ratio, BHJ OSC's were fabricated, and the photovoltaic properties of the devices were investigated. The device characteristics are discussed in terms of the molecular structure, polymer purity, charge-carrier mobility, and film morphology of the blend.

RESULTS AND DISCUSSION

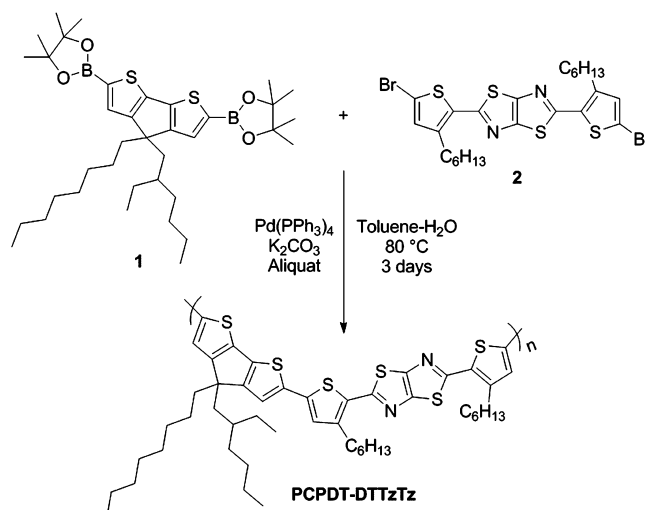
Synthesis and Characterization. The cyclopentadithiophene building block was synthesized using a method recently developed in our group (Scheme 1).³⁰ This three-step synthetic protocol allows to synthesize asymmetrically disubstituted CPDT units. As the side chains are of crucial importance for

Scheme 1. Three-Step Synthetic Approach to Asymmetrically Functionalized 4*H*-Cyclopenta[2,1-*b*:3,4-*b'*]dithiophenes



the final opto-electronic features of the low bandgap material,^{28,32–34} with a major impact on blend morphology, flexibility in the design of the side chains is of high value. In this procedure, variability is introduced at the stage of the ketone derivative. With the aim of balancing polymer crystallinity (toward high charge-carrier mobility) and solubility/processability (toward optimum blend morphology), a CPDT building block with a linear octyl and a branched 2-ethylhexyl side chain was prepared. CPDT-bisboronate monomer **1** (Scheme 2),

Scheme 2. Synthesis of the PCPDT-DTTzTz Narrow Bandgap Polymer



required for Suzuki polycondensation,³⁵ was synthesized by lithiation of the dibrominated CPDT precursor and reaction with 2-isopropoxy-4,4,5,5-tetramethylether-1,3,2-dioxaborolane.

The complementary dibromo-TzTz monomer, 2,5-bis(3'-hexylthiophene-2'-yl)thiazolo[5,4-*d*]thiazole (**2**), was obtained through a condensation reaction between 3-hexylthiophene-2-carbaldehyde and dithiooxamide and subsequent dibromination with *N*-bromosuccinimide (NBS).^{31,36} The additional hexyl side chains on both thienyl constituents were introduced to improve solubility. The PCPDT-DTTzTz copolymer was then produced by means of a Suzuki polymerization reaction in toluene (Scheme 2).^{7,35} End-capping was performed by sequential addition of phenylboronic acid and bromobenzene. The polymer was purified by successive Soxhlet extractions (with methanol, *n*-hexane, and CHCl₃, respectively) and finally precipitated from methanol as a dark, almost black powder. The material was found soluble in a number of common organic solvents such as chloroform, chlorobenzene, and tetrahydrofuran. The number-average molecular weight (*M_n*) after purification, as determined by analytical size exclusion chromatography (SEC) in tetrahydrofuran, was 1.7×10^4 g/mol, with a polydispersity (PDI) of 2.9. Reproducibility of the

Suzuki polycondensation reaction was satisfactory, as similar molecular weights and PDI's were observed for two other polymerization trials.

Thermogravimetric analysis (TGA) experiments in inert atmosphere showed degradation sets in at 400 °C (Figure S1). No weight loss was observed up to 350 °C. Differential scanning calorimetry (DSC) experiments from rt up to 300 °C at a heating rate of 20 K/min (after cooling from 300 °C at the same rate) showed a small step in heat capacity around 10 °C (0.05 J/g·K), followed by a broad exotherm (1 J/g) that gradually evolved to a broad endotherm with a peak maximum at 262 °C (11 J/g) (Figure 1, Table 1). These events can be

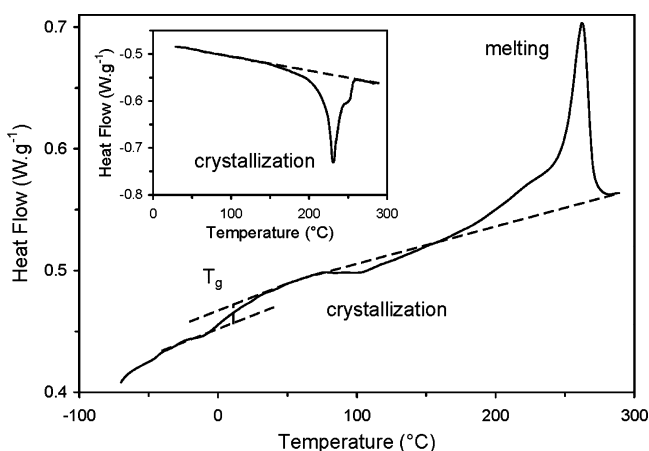


Figure 1. Thermal behavior of PCPDT-DTTzTz as measured by DSC at 20 K/min (after cooling at the same rate).

Table 1. Thermal, Electrochemical, and Optical Properties of PCPDT-DTTzTz

| T_g (°C) | T_m (°C) | T_c (°C) | T_d (°C) | HOMO (eV) | LUMO (eV) | E_g^{EC} (eV) | E_g^{OP} (eV) ^a |
|---------------|---------------|---------------|---------------|--------------|--------------|--------------------|---------------------------------|
| 10 | 262 | 231 | 400 | −5.31 | −3.51 | 1.80 | 1.79 |

^aIn film.

attributed to a glass transition, cold crystallization and crystal reorganization, and melting of the crystals, respectively. Upon cooling at 20 K/min, a crystallization peak was seen with a maximum at 231 °C (10 J/g). Summarily, DSC experiments indicated the polymer is semicrystalline, showing a small T_g and a broad melting endotherm. To confirm this semicrystallinity, XRD analysis of the polymer powder was performed. The XRD spectrum (Figure 2) showed the presence of some crystalline phase, as demonstrated by the appearance of several broad peaks. For a series of four alternating CPDT-based copolymers different from the ones synthesized here, Shim et al.¹⁹ found glass transition temperatures of 103–107 °C. No indications of the presence of a crystalline phase were mentioned in those cases.

UV–vis absorption spectra of the polymer in solution (CHCl_3) and film are plotted in Figure 3. Intramolecular charge transfer between the electron rich CPDT and the electron poor TzTz units in the polymer backbone induces a narrow bandgap and a reasonably broad absorption that covers the 450–700 nm range. In chloroform, the spectrum showed a maximum absorption at 580 nm (with a vibronic shoulder at the low-energy side). In film, the peak bandwidth was broader, and a noticeable fine-structure appeared at the high-wavelength side,

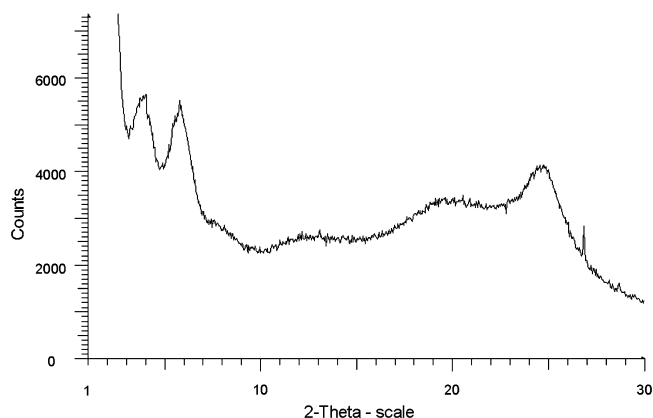


Figure 2. XRD pattern for the PCPDT-DTTzTz copolymer.

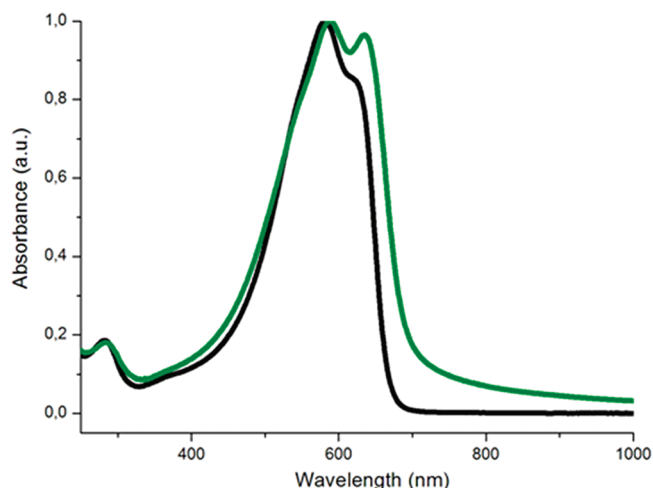


Figure 3. UV–vis absorption spectra of PCPDT-DTTzTz in chloroform solution (black) and in film (green).

suggesting local structural order. The optical bandgap in film was determined to be around 1.79 eV (Table 1). Compared to the well-known bis(2-ethylhexyl)-substituted PCPDTBT donor polymer (E_g 1.46 eV),⁶ the optical bandgap is significantly larger and the overlap with the solar spectrum is somewhat reduced, in particular at the near-IR side.

The cyclic voltammogram (Figure S2) of a thin film of PCPDT-DTTzTz displayed quasi-reversible oxidation and reduction processes during the first potential scan. Upon repeated scanning, the currents associated with these features reduced slowly. The onsets of oxidation and reduction occurred at 0.38 V and −1.42 V vs Ag/AgNO₃, respectively. The corresponding energy levels for the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are −5.31 eV and −3.51 eV, respectively, very close to the values reported by Brabec et al. for PCPDTBT (−5.3 and −3.57 eV).⁴ The resulting electrochemical bandgap is 1.80 eV. This value is almost identical to the observed optical bandgap (1.79 eV) (Table 1).

BHJ Organic Solar Cells. When the PCPDT-DTTzTz polymer, as obtained after Soxhlet extraction and precipitation (batch A), was blended with PC₇₁BM in a 1:3 w/w ratio (in chlorobenzene), the resulting solar cell device (ITO:PEDOT/PSS:active layer:Ca–Ag) showed a moderate performance with an open circuit voltage (V_{oc}) of 0.58 V, a fill factor (FF) of 0.47, a short-circuit current density (J_{sc}) of 9.0 mA/cm², and a

resulting PCE of 2.43% under air mass 1.5 global illumination conditions (AM 1.5G; 100 mW/cm²) (Table 2, Figure 4).

Table 2. OSC Performances of PCPDT-DTTzTz

| batch | M_n (g/mol) | PDI | V_{oc} (V) | J_{sc} (mA/cm ²) | FF | PCE (%) |
|-------|-------------------|-----|--------------|--------------------------------|------|---------------------|
| A | 1.7×10^4 | 2.9 | 0.58 | 9.0 | 0.47 | 2.43 ^a |
| B | 1.7×10^4 | 2.3 | 0.63 | 10.33 | 0.51 | 3.34 ^b |
| C | 1.5×10^4 | 2.2 | 0.63 | 10.37 | 0.54 | 3.50 ^b |
| D | 1.4×10^4 | 2.4 | 0.67 | 11.13 | 0.54 | 4.03 ^{b,c} |

^aUnpurified polymer. ^bPurification by preparative SEC. ^cMixture of B and C in 1:2 ratio.

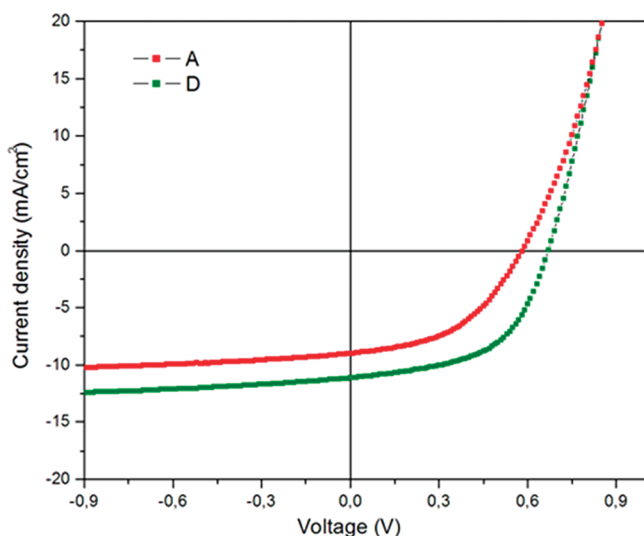


Figure 4. *J*-*V* characteristics of photovoltaic devices fabricated from different batches of PCPDT-DTTzTz (blended with PC₇₁BM in a 1:3 w/w ratio).

As polymer molecular weight (distribution) and purity are essential parameters influencing the opto-electronic properties and the final solar cell outcome, purification and fractionation of the PCPDT-DTTzTz copolymer were pursued by preparative SEC. An additional advantage of this technique is that it can somehow remediate the significant batch-to-batch variations often observed for transition-metal catalyzed polymerization reactions (mainly Suzuki/Stille). Unfortunately, limited solubility of the material (at a concentration of 20 mg/2 mL) in the eluent (CHCl₃) somewhat hampered effective fractionation due to polymer aggregation (see Figures S3 and S4). Two purified polymer fractions (B and C, Table 2) were obtained, with slightly varying M_n and PDI. Solar cell devices constructed from these materials showed a significant increase in PCE of more than 1% (to 3.5% for batch C, Table 2), by noticeable improvement of all three parameters (V_{oc} , J_{sc} , and FF). Upon mixing both purified batches (batch D = 1:2 ratio of B and C, Table 2), mainly affecting the PDI, the solar cell performance was even further improved, showing a PCE of 4.03% (V_{oc} 0.67 V, FF 0.54, J_{sc} 11.13 mA/cm²) (Table 2, Figure 4). As the experimentally observed V_{oc} fits rather well with the theoretically expected value, the PCE seems to be V_{oc} limited for this material.^{4,6} The PCE was noticeably higher than for a series of four different PCDT-X:PC₆₁BM combinations earlier reported by Shim and co-workers.¹⁹

The thin film morphology of the BHJ mixture was examined by atomic force microscopy (AFM) and transmission electron

microscopy (TEM) (Figure 5). The purified PCPDT-DTTzTz polymer formed homogeneous, well-distributed blend films

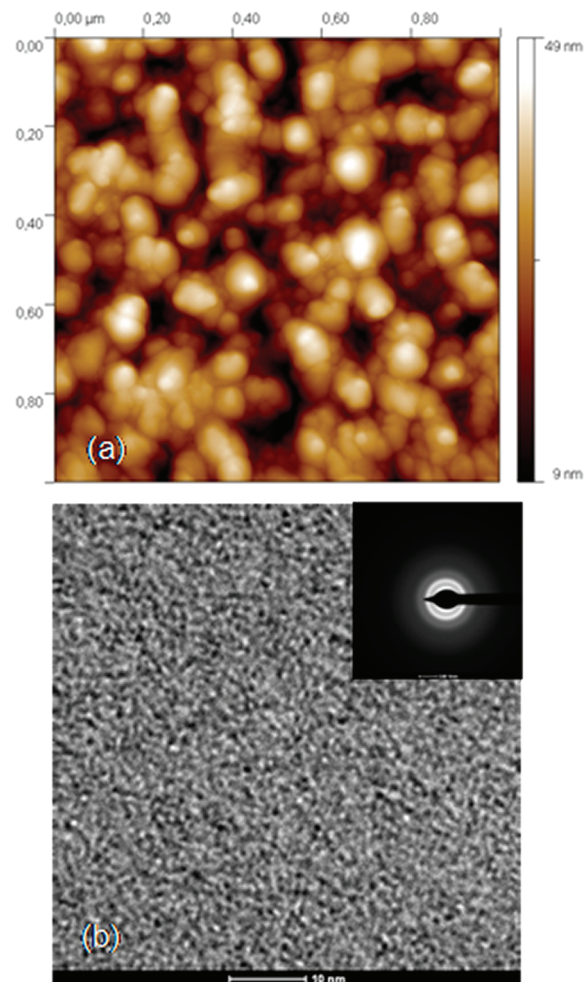


Figure 5. Topographic AFM images of spin-coated PCPDT-DTTzTz:PC₇₁BM films (measurements on a solar cell device), with a rms roughness value of 7.3 nm (1 μ m \times 1 μ m) (a) and BFTEM-image (with diffraction pattern in inset) of the PCPDT-DTTzTz:PC₇₁BM (1:3) film (b).

with PC₇₁BM, indicating good miscibility (or compatibility) with phase segregation on the nanometer scale.

Thin-Film Transistors (TFTs). To relate the relatively high short-circuit current density to polymer mobility, thin-film transistors were prepared from the purified polymer batch (D). The PCPDT-DTTzTz copolymer exhibited typical *p*-channel TFT characteristics. Output and transfer curves are displayed in Figure 6. The field-effect mobility, calculated in the linear regime, was found to be 1.0×10^{-3} cm²/(V s), 1 order of magnitude higher than reported values in literature for different TzTz-based copolymers,¹⁹ and hence in good agreement with the photovoltaic properties. In addition, the transfer curves of the PCPDT-DTTzTz material exhibited a small threshold voltage (V_{th}) around -14 V. The small hysteresis suggests a high degree of purity.

CONCLUSION

We have synthesized a novel performant poly[(4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene)-*alt*-(2,5-dithienylthiazolo[5,4-*d*]thiazole)] narrow bandgap copolymer PCPDT-DTTzTz, with

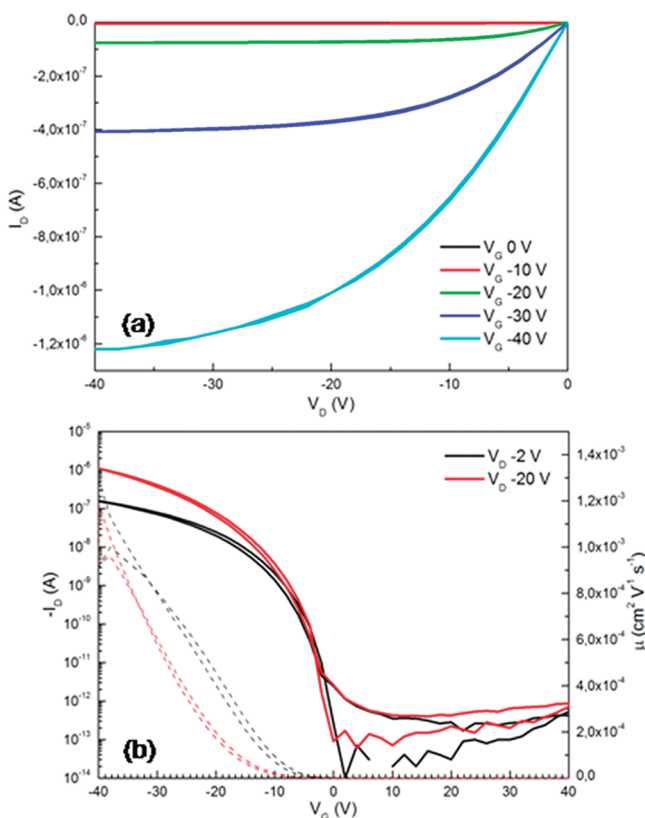


Figure 6. (a) Output curves for various gate biases. The gate bias was changed in 10 V steps from 0 V to -40 V. (b) Linear and saturated transfer characteristics of a PCPDT-DTTzTz transistor. The channel length and width were 10 and $2500 \mu\text{m}$, respectively. The extracted mobilities were around $1.0 \times 10^{-3} \text{ cm}^2/(\text{V s})$.

asymmetrical alkyl substitution on the CPDT building blocks and additional hexyl side chains on the thienyl subunits of the TzTz constituents. Addition of these extra substituents improved the solubility, on one hand, and, on the other hand, triggered the stacking tendency of the polymer resulting in a semicrystalline material. After purification by preparative SEC, the polymer showed a hole mobility of $1.0 \times 10^{-3} \text{ cm}^2/(\text{V s})$ and organic solar cells constructed with a PCPDT-DTTzTz:PC₇₁BM active layer afforded a photovoltaic power conversion efficiency of 4.03% (without extensive optimization work). A noticeable increase in efficiency of more than 1% was obtained upon purification. The presented results clearly stress the crucial effects of the (alkyl) functionalization pattern and material purity on the photovoltaic performance of low bandgap polymer materials.

EXPERIMENTAL SECTION

Materials and Methods. NMR chemical shifts (δ , in ppm) were determined relative to the residual CHCl_3 absorption (7.26 ppm) or the ^{13}C resonance shift of CDCl_3 (77.16 ppm). Gas chromatography–mass spectrometry (GC–MS) analyses were carried out applying Chrompack Cpsil5CB or Cpsil8CB capillary columns. Molecular weights and molecular weight distributions were determined relative to polystyrene standards (Polymer Laboratories) by analytical size exclusion chromatography (SEC). Chromatograms were recorded on a Spectra Series P100 (Spectra Physics) equipped with two mixed-B columns ($10 \mu\text{m}$, $0.75 \text{ cm} \times 30 \text{ cm}$, Polymer Laboratories) and a refractive index detector (Shodex) at 40°C . THF was used as the eluent at a flow rate of 1.0 mL/min . Preparative SEC was performed on JAIGEL 2H and 2.5H columns attached to a LC system equipped

with a UV detector (path 0.5 mm) and a switch for recycling and collecting the eluent (CHCl_3 ; flow rate 3.5 mL/min and injection volume 1.0 mL).

Solution UV–vis absorption measurements were performed with a scan rate of 600 nm/min in a continuous run from 200 to 800 nm . Thin film electrochemical measurements were performed with an Eco Chemie Autolab PGSTAT 30 Potentiostat/Galvanostat using a conventional three-electrode cell under N_2 atmosphere (electrolyte: 0.1 M TBAPF_6 in anhydrous CH_3CN). For the measurements, a Ag/AgNO₃ reference electrode (0.01 M AgNO_3 and 0.1 M TBAPF_6 in anhydrous CH_3CN), a platinum counter electrode, and an indium tin oxide (ITO) coated glass substrate as working electrode were used. The polymers were deposited by drop-casting directly onto the ITO substrates. Cyclic voltammograms were recorded at 50 mV/s . From the onset potentials of the oxidation and reduction the position of the energy levels could be estimated. All potentials were referenced using a known standard, ferrocene/ferrocenium, which in CH_3CN solution is estimated to have an oxidation potential of -4.98 eV vs vacuum. DSC measurements were performed at 20 K/min in aluminum crucibles on a TA Instruments Q2000 Tzero DSC equipped with a refrigerated cooling system (RCS), using nitrogen (50 mL/min) as purge gas. TGA experiments were performed at 50 K/min in platinum crucibles on a TA Instruments Q5000 TGA using nitrogen (50 mL/min) as purge gas. The XRD measurements were performed with a Bruker D8 discover diffractometer under θ - 2θ conditions. The system worked in parafocusing geometry using a Göbel mirror (line focus, mostly $\text{CuK}\alpha 1$ and $\text{CuK}\alpha 2$ rays). The X-rays were detected by a 1D detector.

Polymer solar cells were fabricated by spin-coating a PCPDT-DTTzTz:PC₇₁BM (Solenne) blend in a 1:3 w/w ratio, sandwiched between a transparent anode and an evaporated metal cathode. The transparent anode was an ITO covered glass substrate which was coated with a 30 nm poly(3,4-ethylenedioxythiophene)/poly(styrene-sulfonic acid) PEDOT/PSS (CLEVIO P VP.AI 4083) layer applied by spin-coating. The ITO glass substrate was cleaned by ultrasonification (sequentially) in soap solution, deionized water, acetone, and isopropanol. The cathode, a bilayer of 50 nm Ca and 100 nm Ag , was thermally evaporated. PCPDT-DTTzTz and PC₇₁BM (1:3 w/w ratio) were dissolved together in chlorobenzene to give an overall 40 mg/mL solution, which was stirred overnight at 80°C inside a glovebox. Solar cell efficiencies were characterized under simulated 100 mW/cm^2 AM 1.5 G irradiation from a Xe arc lamp with an AM 1.5 global filter. Topography of the solar cells was studied by AFM, using a Picoscan PicoSPM LE scanning probe in tapping mode. The active layer morphology was studied with TEM (FEI Tecnai Spirit using an accelerating voltage of 120 kV).

Transistors were fabricated using heavily doped n -type Si wafers as bottom gate electrodes with a 200 nm thermally oxidized SiO_2 layer as the bottom gate dielectric. Au source and drain electrodes were defined by photolithography on a 2 nm Ti adhesion layer. The SiO_2 layer was passivated with hexamethyldisilazane prior to semiconductor deposition. The semiconducting active layer (30 nm) was spin-coated from a $0.5 \text{ wt } \%$ polymer solution in chlorobenzene. Before measurements, the substrates were annealed in vacuum at 100°C . The measured transistors had a channel width (W) of $2500 \mu\text{m}$ and a channel length (L) of $10 \mu\text{m}$. Electrical characterization was carried out in vacuum with an Agilent 4155C semiconductor parameter analyzer. Transistor performance was mainly evaluated by the thin film mobility (μ_{th}) extracted in the linear regime and by the threshold voltage (V_{th}).

Synthesis. Unless stated otherwise, all reagents and chemicals were obtained from commercial sources and used without further purification. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was purchased from Acros Organics. THF was dried by distillation from Na/benzophenone. 4-(2'-Ethylhexyl)-4-octyl-4H-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene and 2,5-bis(5'-bromo-3'-hexylthiophene-2'-yl)thiazolo[5,4-*d*]thiazole (**2**) were synthesized according to previously reported procedures.^{30,31} Material identity and purity were confirmed by MS, ^1H and ^{13}C NMR.

2,6-Dibromo-4-(2'-ethylhexyl)-4-octyl-4H-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene. Protected from light, a solution of NBS (0.94 g , 5.3

mmol) in DMF (50 mL) was added dropwise to a solution of 4-(2'-ethylhexyl)-4-octyl-4H-cyclopenta[2,1-b:3,4-b']dithiophene (1.00 g, 2.5 mmol) in DMF (65 mL), after which the mixture was stirred overnight at rt. Subsequently, the mixture was poured onto ice and extracted with diethyl ether (3 × 100 mL). The combined organic layers were washed with NaHCO₃ (sat) and brine, dried over MgSO₄, and concentrated by evaporation *in vacuo*. The crude solid was purified by column chromatography (silica, eluent *n*-hexane). The compound was obtained as a slightly yellow oil (0.91 g, 65%). ¹H NMR (300 MHz, CDCl₃) δ 6.94 (s, 1H), 6.93 (s, 1H), 1.83 (t, *J* = 4.8 Hz, 2H), 1.78–1.72 (m, 2H), 1.27–0.89 (m, 21H), 0.86 (t, *J* = 7.1 Hz, 3H), 0.79 (t, *J* = 6.9 Hz, 3H), 0.64 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 155.9/155.8, 136.6/136.5, 125.0/124.9, 111.05/111.0, 55.1, 41.6, 39.4, 35.5, 34.1, 31.9, 30.0, 29.43, 29.40, 28.6, 27.4, 24.4, 22.9, 22.8, 14.3, 14.2, 10.8; GC-MS (EI) *m/z* 558/562 [M⁺].

2,2'-[4-(2'-Ethylhexyl)-4-octyl-4H-cyclopenta[2,1-b:3,4-b']-dithiophene-2,6-diyl]-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (1). A *n*-BuLi solution (1.1 mL, 2.5 M in hexanes) was added at −78 °C to a solution of the dibromo-CPDT precursor (260 mg, 0.46 mmol) in dry THF (20 mL) under inert atmosphere. The mixture was stirred for 30 min at −78 °C, after which 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.5 mL, 0.46 g, 2.4 mmol) was added at −78 °C. The reaction was allowed to reach rt overnight. The reaction mixture was then poured out in water and diisopropyl ether, and the organic layer was washed with brine. The solvents were evaporated from the organic layer, and the resulting oil was subjected to preparative SEC in CHCl₃. This resulted in the isolation of the diboronic ester **1** (0.201 g, 67%) as a slightly yellow sticky oil. ¹H NMR (400 MHz, CDCl₃) δ 7.43 (s, 1H), 7.41 (s, 1H), 1.86 (t, *J* = 5.0 Hz, 2H), 1.80–1.76 (m, 2H), 1.35/1.34 (s, 21H), 1.25–0.90 (m, 21H), 0.84 (t, *J* = 7.0 Hz, 3H), 0.73 (t, *J* = 7.0 Hz, 3H), 0.59 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 161.4/161.2, 144.1/144.0, 131.6/131.5, 130.0, 84.1, 52.8, 41.8, 39.6, 35.4, 33.8, 31.9, 30.1, 29.4, 28.4, 27.5, 24.9, 24.83, 24.75, 24.4, 22.9, 22.7, 14.2, 10.7; MS (CI) *m/z* 655 [M⁺].

Poly([4-(2'-ethylhexyl)-4-octyl-4H-cyclopenta[2,1-b:3,4-b']-dithiophene-2,6-diyl]-alt-[2,5-di(3'-hexylthiophen-2'-yl)thiazolo-[5,4-d]thiazole-5',5''-diyl]) (PCPDT-DTTzTz). CPDT monomer **1** (0.049 g, 78 μmol), TzTz monomer **2** (0.051 g, 78 μmol), K₂CO₃ (0.76 mL, 2 M), and 1 drop of Aliquat 336 were gathered in a mixture of toluene (1.5 mL) and water (0.35 mL). The solution was purged with argon for 30 min, and then Pd(PPh₃)₄ (0.009 g, 8 μmol, 10 mol %) was added. The reaction was stirred at 80 °C under an inert atmosphere for 3 days. Subsequently, a toluene solution of phenylboronic acid (0.010 g, 85 μmol) was added, followed by the addition of bromobenzene (0.009 mL, 85 μmol), and the mixture was stirred overnight at 80 °C. The resulting mixture was then poured into a mixture of methanol and water (2:1, 200 mL) and stirred overnight. The precipitated dark solid was recovered by filtration, redissolved in CHCl₃ (20 mL), and added dropwise to methanol (200 mL). The precipitated solid was filtered off (PTFE membrane 47 mm/0.45 μm) and subjected to successive Soxhlet extractions for 24 h with methanol, *n*-hexane, and CHCl₃, respectively. After evaporation, the polymer residue was redissolved in CHCl₃ and precipitated again from methanol, filtered, washed with methanol, and dried, affording PCPDT-DTTzTz as a black powder (0.045 g, 64%). ¹H NMR (400 MHz, CDCl₃) δ 7.16 (br, 2H), 6.79 (br, 2H), 2.95 (br, 2H), 2.80 (br, 2H), 1.43–1.25 (m, 44H), 1.00–0.85 (m, 18H); UV–vis (CHCl₃, nm) λ_{max} 580; UV–vis (film, nm) λ_{max} 588/635; SEC (THF, PS standards) *M*_n = 1.7 × 10⁴ g/mol, *M*_w = 5.0 × 10⁴ g/mol, PDI = 2.9.

■ ASSOCIATED CONTENT

Supporting Information

TGA curve and cyclic voltammogram of PCPDT-DTTzTz, preparative size exclusion chromatograms indicating polymer aggregation, and ¹H and ¹³C NMR spectra of the CPDT and TzTz precursors. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors gratefully acknowledge the IWT (Institute for the Promotion of Innovation by Science and Technology in Flanders) for their financial support via the SBO-project 060843 "PolySpec". We also acknowledge the European ONE-P project for grant agreement no. 212311 which facilitates the IMEC-IMOMEC/High Tech Campus Eindhoven collaboration. NvdB and W.M. thank the FWO (Fund for Scientific Research – Flanders) for a doctoral and postdoctoral research mandate, respectively. Special thanks go out to Hugette Penxten for performing the cyclic voltammetry measurements.

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